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(Art 34 Entered)OIL FOR AGRICULTURAL USE

This applⁿ is a 371 of FIELD OF THE INVENTION PCT/AU96/00189 filed 4/2/96.

1 The present invention relates to an oil for agricultural use, in particular to a petroleum derived spray oil "PSO", being primarily an oil for use as an insecticide and/or an acaricidal control spray oil. More particularly, the invention relates to a PSO having certain additive(s) which reduces the phytotoxicity of the oil in relation to, for example, crops and plants.

10 The invention will be primarily described in relation to its use with refined and semi-refined light oils, but it should be appreciated that the invention has broader application.

BACKGROUND ART

15 Petroleum spray oils ("PSO's") are used in agriculture on their own and as carriers or solvents for spraying pesticides, herbicides, micronutrients, chemical adjuvants, etc. The oils are widely used because of their effectiveness in controlling a wide range of pests and diseases, and because of their relatively low cost,

20 relatively low health hazard (including low mammalian toxicity) and wide availability. They also show an absence of residual effect against beneficial predators and parasitoids.

25 However, certain grades and applications of PSO's have been shown to be phytotoxic, particularly in high dosage applications, or in environments where exposure to sunlight is imminent or intense. Acute phytotoxicity can lead to excessive leaf drop in plants and less obvious chronic symptoms such as inhibition of yield of crops.

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There has been much debate in the scientific literature as to the mechanisms of oil induced

phytotoxicity, but a primary source of phytotoxicity has been attributed to membrane disruption. Membrane disruption involves the dissolution of folia semipermeable membranes, leading to a breakdown in the plant structure and wilting and/or death of the plant. The problem of membrane disruption was largely overcome by improved oil refinement and the instigation of quality criteria.

Phytotoxic effects have been linked with the distillation temperature or viscosity of the particular oil used in spraying. Phytotoxicity has also been attributed to spray oil dose rate and duration of spraying.

However, photodegradation of modern highly refined PSO's with subsequent phytotoxicity has largely been overlooked by researchers and manufacturers in this area.

The formation of acids in PSO's is associated with the photo-degradation (eg. oxidation) of the PSO mediated by UVA radiation. It is now surmised that a contributing or major factor in the phytotoxicity of PSO's could relate to the level of acidity in the PSO when sprayed, or developed after spraying. Even "superior" spray oils (ie. highly refined spray oils), upon exposure to light, may develop acidity and become markedly phytotoxic. This tendency can be enhanced where an oil applied to a plant is exposed to UV radiation (eg. sunlight) for an extended period of time, so that many of the components of the oil are photo-oxidised into organic acids, in turn attacking the plants.

It would be advantageous if at least preferred embodiments of the present invention provided an oil for agricultural use, in particular an oil for agricultural spraying, that includes therein a component, or components, capable of preventing the formation of acidic products within the oil, or ameliorating or neutralising their effects.

SUMMARY OF THE INVENTION

In a first aspect, the present invention provides an agricultural spray oil having added thereto an oil soluble basic compound that is selected from one or more of:

- (a) a sulphonate;
- (b) a phenate;
- (c) an alkyl-amine.

By employing such an oil soluble basic compound, at least some of any acidic compounds present in or formed in the oil in use can be neutralised.

Preferably the sulphonate and phenate are respectively overbased sulphonates or phenates, and it is particularly preferred that the sulphonate is a calcium overbased sulphonate.

Preferably, the calcium overbased sulphonate is present in the oil in a range 0.01-5 wt% total. It is most preferred that the calcium overbased sulphonate is present in the oil in an amount of about 1.0 wt% total. A metal overbased sulphonate includes an aqueous micelle defined by a plurality of relatively long-hydrocarbon chain molecules having a polar head (ie. sulphonate functionality) and a hydrophobic tail (eg. long chain alkyl) and an excess amount of metal base (eg. calcium carbonate) in the micelle. (A depiction of an overbased sulphonate is shown in Figure 5). Metals other than calcium can also be used in the sulphonate or phenate (eg. magnesium overbased sulphonates).

As described above, exposure of a PSO to UV radiation brings about photo-degradation of the PSO (ie. through the photo-oxidation thereof) into peroxides, acids, esters, polymers etc, thus increasing the phytotoxicity of the PSO.

In a second aspect, the present invention provides an agricultural spray oil having added thereto an oil

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soluble UV deactivator that is selected from one or more of:

- (a) a benzotriazole UV absorber;
(b) a zinc diamyldithio carbamate; or
5 (c) a benzoxazole, benztriazole or benzthiazole compound, but excluding the compound 2-mercaptobenzothiazole.

Photo-oxidation can thus be prevented or ameliorated, or alternatively any photo-oxidation
10 products (eg. peroxide free-radicals) may be scavenged and/or trapped.

The UV absorber absorbs UV radiation and thus tends to prevent photo-oxidation, whereas the free-radical trap or scavenger neutralises any free-radicals produced
15 during photo-oxidation (eg. peroxides).

Preferably, the UV absorber is TINUVIN 171, pref. at 0.005%. (Trade mark of Ciba Geigy).

Alternatively, the UV absorber can be iso-octyl-3-(3-(2H-benzotriazole-2-yl)-5-tert.butyl-4-hydroxyphenyl)
20 propionate. (A commercially available form of this compound is known as TINUVIN 384 (Trade Mark of Ciba Geigy Limited). TINUVIN 384 is a liquid UV absorber of the hydroxyphenyl benztriazole class. It has high thermal stability and permanence.

25 Preferably, the iso-octyl-3-(3-(2H-benzotriazole-2-yl)-5-tert.butyl-4-hydroxyphenyl) propionate is present in the range of 0.001-0.5 wt% total of the oil, most preferably at about 0.01 wt% total of the oil.

30 The free-radical trap or scavenger is zinc diamyldithiocarbamate.

A preferred oil for use as a PSO is a refined light oil (C₁₅ to C₃₅ length of hydrocarbon chain). In particular, it is preferred that the oil portion of the
35 PSO is a C₁₅ to C₃₅ light paraffinic or light naphthenic petroleum derived oil.

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Preferably, the light paraffinic or light naphthenic
boil is:

- (a) chemically neutralised;
- (b) clay treated;
- 5 (c) solvent refined; or
- (d) hydro-treated.

Physical properties of such oils are shown in Tables
2 and 3.

10 Surfactants are typically added to PSO's to enable
the oil to be dispersed in water for subsequent spraying.
Typical surfactants include nonionic surfactants. The
nonionic surfactants can be added in the range of 0.5 wt%
to 20 wt%.

15 In a most preferred spray oil formulation, a refined
light oil can include 0.5 - 20 wt% nonionic surfactant,
1.0 wt% calcium overbased sulphonate and 0.005 wt%
benztriazole compound. Thus, preferred formulations may
include both an oil soluble basic compound and a UV
deactivator.

20 In a further aspect of the present invention an
additive composition for an oil for agricultural use is
provided which can include a base (as defined above),
and/or a UV deactivator (as defined above).

25 This additive composition can also include
emulsifying surfactant(s) (as defined above). Such an
additive composition can be provided separately from the
oil (eg. PSO) and can be added to the oil in situ (eg.

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prior to spraying). The additive composition finds useful application when added to less than ideally refined oils, or oils that are in various stages of oxidation, and can stabilise, eliminate or reduce the phytotoxicity of such oils prior to spraying etc.

BRIEF DESCRIPTION OF THE DRAWINGS

Notwithstanding any other forms which may fall within the scope of the present invention, preferred forms of the invention will now be described, by way of example, and also in conjunction with the attached Figures in which:

Figure 1 shows the effect of acidity on betacyanin efflux and the control thereof by adding calcium overbased sulphonate to oils (with reference to oils without such addition);

Figures 2 and 4 show the effect of adding a base and UV deactivator to different oils when exposed to UV radiation;

Figure 3 shows a fourier transform infra-red carbonyl peak measurement (ie. measurement of acidity) for different oils with base and/or UV deactivator added thereto;

Figure 5 depicts schematically typical molecular structures of sulphonates and phenates;

Figure 6 shows the UV absorption spectra of typical 2-hydroxybenzophenones (as preferred UV deactivators);

Figure 7 shows schematically the molecular structure of TINUVIN 384; and

Figure 8 shows the transmission spectrum for various solution concentrations of TINUVIN 384 in toluene.

MODES FOR CARRYING OUT THE INVENTION

Some non-limiting examples of preferred embodiments of the invention will now be described.

EXAMPLES

5 A standard nomenclature has been employed throughout the examples for the petroleum spray oils. For example, when a PSO is referred to as a 60N or 70N oil, the number portion refers to and is derived from the measurement of viscosity in Saybolt universal seconds and the term neutral (N) refers to the paraffinic nature of the oil.

10 When the terminology ASTM and AS is used throughout the specification it is a reference to American Society for Testing and Materials and Australian Standard respectively.

15 Membrane disruption (and thus phytotoxicity), as referred to in the Figures has been measured by the Betacyanin Efflux Test. The standard test is applied on beetroot tuba disks which have no cuticle and thus the effects of a PSO on the cell membrane can be monitored directly.

20 MEMBRANE DISRUPTION BY BETACYANIN EFFLUX FROM UNPROTECTED CELL MEMBRANES

Oil induced disruption of cell membranes unprotected by a cuticle layer was measured by betacyanin efflux from beetroot tuba disks (Coupland, D. et. al. (1989)
25 Evaluation of three techniques used to determine surfactant phytotoxicity; Annals of Applied Biology 115, 147-156). Test material was prepared by making 7 mm diameter disks with a cork borer and cutting them to 1 mm thickness. Preliminary studies showed disks were best
30 used after a two hour rinse in tap water followed by air drying. It was essential to remove adsorbed water because water induced premature betacyanin efflux.

Dry disks (n=3) of known fresh weight were added to 10 mL test tubes and completely covered by 2 Ml oil. The

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treatments were then incubated for 3 hours at 30°C when an isotonic solution of 5 Ml of 0.4 M sorbitol in deionised water was added. The tubes were set aside to allow betacyanin efflux for 18 hours at 20°C. Analysis of the aqueous layer was performed by colorimetric analysis at 535 nm in 1 cm cells against a solvent blank. Absorbance readings were then normalised to absorbance/disk weight to eliminate differences between disks. This procedure together with the choice of three randomly chosen disks was successful in obtaining reproducible results. Cooking of the disks to produce a maximum efflux for normalisation purposes did not improve the precision.

The pink colour developed by betacyanin efflux conformed to a classical logistic curve when calibrated with oil acidity. The effective dose (ED₅₀) for 3 hours contact was 0.11 mg KOH/g oil (ASTM D927) and the detection limit for no observable effect was 0.08 mg KOH/g oil (0.5 Abs units/g).

In the Figures and Tables, the phytotoxicity of various spray oils, as determined by betacyanin efflux, is shown.

From the tests, it was established that when a membrane disruption value of 0.5 Absorbance Units/g specimen (Abs/g) was exceeded, then damage to the plant would follow. In other words, a result of 0.5 or less is a phyto-safe membrane disruption value.

Example 1 (Figure 1)

Various levels of calcium overbased sulphonate, (shown as "base" in Figure 1) were added to 70N and 150N oils, both oxidised and unoxidised. As shown clearly in Figure 1, with the addition of both 0.1% of the base and 1% of the base, the membrane disruption value is held below about 0.4 Abs/g (which is in the phyto-safe zone). Figure 1

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also compare these oils against standard oils of different acid values.

Example 2 (Figure 2)

5 A 70N oil had a number of additives (as shown in Figure 2) added thereto. Figure 2 shows the effects of exposing the oil to 4mW of UV radiation/cm² with time, and also indicates the effects of variation in the levels of base (eg. calcium overbased sulphonate) and UV deactivator (eg. TINUVIN 384).

10 Example 3 (Figure 3)

15 A 70N oil (with similar additives to Example 3) was exposed to 4mW of UV radiation/cm². Figure 3 shows the results from a fourier transform infra-red spectrum of the oil with time, indicating the variation in acidity between various "treated" and "untreated" oils. From Figure 3, it can be seen that the addition of even a small amount of base and UV deactivator minimises the formation of acids (indicated by the carbonyl function, ie. absorbance at 1710 cm⁻¹).

20 Example 4 (Figure 4)

25 In a similar manner to Example 2, a 70N oil had a number of additives added thereto and was then exposed to UV radiation. The acidity of the resultant oil with time is shown for various combinations of the base and UV deactivator, indicating that excellent results are obtained when both a base and a UV deactivator are present.

Example 5

30 Various additive compositions for use as a separate additive or concentrate pack for addition to oils for agricultural use were prepared. The additive compositions most typically included one or two nonionic

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surfactants (ie. emulsifying surfactants to render the oil suitable for use as a PSO (eg. in water)), and an oil soluble base (eg. calcium overbased sulphonate) and/or a UV deactivator (eg. TINUVIN 384).

- 5 An advantage of an additive composition is that it can be added to PSO's in situ (ie. it can be transported in a concentrate form to the user of the PSO, who then adds an appropriate dosage). This means that a local or regional oil can be employed (ie. the treated oil itself
10 does not need to be transported to site) and thus transportation costs can be reduced.

A most preferred additive composition was as follows: Nonionic surfactant(s) plus calcium overbased sulphonate and benztriazole compound in a ratio of
15 140.5:1, (not including surfactant).

Example 6

Another preferred formulation for a light petroleum spray oil included 0.5 - 20 wt% nonionic surfactant, 1.0 wt% calcium overbased sulphonate and 0.05 wt% TINUVIN 384.

- 20 Table 1 below summarises the photo-degradation performance of various compositions when added to 60 Neutral oil, 70 Neutral oil and 150 Neutral oil, against these oils by themselves. This Table demonstrates the broad applicability of the formulation in different types
25 of oil, and shows that membrane disruption and acidity are considerably reduced or eliminated when such additives are present.

Table 2 shows the typical chemical characteristics of petroleum spray oils suitable for use with the present
30 invention. Table 3 shows some of the properties of a broad range of light spray oils suitable for use in the present invention. Table 4 shows absorption spectra of a

number of different benzophenones for use as a UV deactivator.

Figure 5

Figure 5 shows a schematic representation of the typical molecular structures of overbased sulphonates and phenates, wherein the micelle is defined by a plurality of water-soluble polar sulphonate functionality groups (hydrophilic heads) facing inwardly, with each sulphonate head having an oil soluble non-polar alkyl chain (hydrophobic tail) projecting outwardly therefrom.

The overbased sulphonates contain an excess amount of metal base (eg. calcium carbonate) which neutralises acids formed during photo-degradation of the oils. The alkyl chain length of the sulphonates ranges from 18 to over 20 carbon atoms, whereas the alkyl chain length of the phenates contains approximately 12 carbon atoms.

Figures 6, 7 and 8

Figure 6 shows the UV absorption spectra of typical 2-hydroxybenzophenones which can be used as a UV deactivator in some forms of the present invention. (Table 4 also shows the absorption spectra of different benzophenones).

Figure 7 shows the chemical structure of TINUVIN 384 and

Figure 8 shows a transmission spectra for various concentrations of TINUVIN in toluene, indicating its preferred usage as a UV absorber.

From the above description, it can be seen that the addition of an oil soluble base and an oil soluble UV deactivator (in various preferred configurations) can eliminate, ameliorate or reduce membrane disruption (as

measured by betacyanin efflux) and acidity in petroleum spray oils (resulting from the photo-degradation/photo-oxidation of spray oils in the presence of oxygen and UV radiation), thereby reducing the phytotoxicity of spray oils.

5 The invention finds application with a wide variety of spray oils, and particularly with less than ideally refined base oils. Thus, by adding a preferred composition to such non-ideally refined spray oils, they
10 can immediately be used thereafter with a reduced risk of phytotoxicity.

Whilst the invention has been described with reference to a number of preferred embodiments, it should be appreciated that the invention can be embodied in many
15 other forms.

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TABLE 1
THE EFFECT OF ADDITIVES IN PETROLEUM SPRAY OIL

| Treatment exposed for 20 hours (@2mW/cm ² UV [a] light) | Betacyanin efflux (Abs/g) | Carbonyl peak (Abs. units) | Acidity mg KOH/g |
|---|------------------------------|-------------------------------|---------------------|
| 60 Neutral oil | 2.45 | 0.1209 | 0.26 |
| 60 Neutral oil + 1% base +0.005% UV deactivator | 0 | 0.0678 | 0.009 |
| 70 Neutral oil | 3.16 | 0.1421 | 0.3 |
| 70 Neutral oil + 1% base +0.005% UV deactivator | 0 | 0.0858 | 0.007 |
| 150 Neutral oil | 2.57 | 0.2118 | 0.77 |
| 150 Neutral oil + 1% base +0.005% UV deactivator | 0 | 0.1395 | 0.26 |

TABLE 2
TYPICAL CHEMICAL CHARACTERISTICS OF PETROLEUM SPRAY OILS

| Analysis | Method | Typical base oil ^A | AS 1888 C21 NR class ^B | AS 1888 C23 NR class ^B |
|------------------------------|---------------------|-------------------------------|-----------------------------------|-----------------------------------|
| Density @ 15°C | ASTM D1298 (g/mL) | .846 | <0.870 | <0.880 |
| Refractive index @ 20°C | ASTM D1218 | 1.4680 | - | - |
| Viscosity @ 40°C | ASTM D2270 (cSt) | 12 | - | - |
| %UR | ASTM D483 | 94 | >92 | >92 |
| Carbon No. @10% ^C | Furness et al. 1987 | 20.2 | >18.2 | >19.0 |
| Carbon No. @50% | " | 23.5 | >21 | >22.0 |
| Carbon No. @90% | " | 25.3 | <24.2 | <26.0 |
| 50% DT | ASTM D2887 | 385°C | >357°C | >369°C |
| 50% DT | ASTM D1160 | 231°C | >206°C | >217°C |
| Boiling range | ASTM D2887 | 57°C | <74°C | <81°C |
| %Cp | ASTM D3238 | 70 | - | - |
| %Cn | " | 28 | - | - |
| %Ca | " | 2 | - | - |
| %Aromatic mass | ASTM D2549 | 10 | - | - |

A = 70 Neutral

B = Proposed Australian standard [Furness et al. 1987]. These classes equate to the USA "superior" oil grade.

C = Carbon Number when X% mass has distilled.

NR = Narrow Range

%Cp = % carbon atoms as paraffin, n = naphthene, a = aromatic

DT = Distillation temperature (C°: @ 101 kPa ASTM D2887 or 10 kPa ASTM D1160).

TABLE 3

Properties of Oils as Defined by the TSCA Inventory^A

| CAS name of distillates | CAS No. | Carbon number distribution | Remarks |
|---|------------|----------------------------|---|
| Chemically neutralized light paraffinic | 64742-28-5 | C15-C30 | Contains relatively large proportion of saturates |
| Chemically neutralized light naphthenic | 64742-35-4 | C15-C30 | Few normal paraffins |
| Clay treated light paraffinic | 64742-37-6 | C15-C30 | Mostly saturates |
| Clay treated light naphthenic | 64742-45-6 | C15-C30 | Few normal paraffins |
| Solvent refined light paraffinic | 64741-89-5 | C15-C30 | Predominantly saturates |
| Solvent refined light naphthenic | 64741-97-5 | C15-C30 | Few normal paraffins |
| Hydrotreated light paraffinic | 64742-55-8 | C15-C30 | Contains a relatively large proportion of saturates |
| Hydrotreated light naphthenic | 64742-53-6 | C15-C30 | Few normal paraffins |

A: US EPA (1978); TSCA, US Toxic substances control act.

B: CAS number: Chemical abstracts service registry number.

TABLE 4

ABSORPTION SPECTRA OF BENZOPHENONES

| Benzophenone (substituents) | a | | b | | c | | Ref. |
|--------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------|
| | λ_{max} | $\log \epsilon$ | λ_{max} | $\log \epsilon$ | λ_{max} | $\log \epsilon$ | |
| None | 250 | 4.30 | — | — | 333 | 1.65 | 89 |
| 4-OH | 248 | 4.00 | 289 | 4.17 | — | — | 114 |
| 4,4'-di-OH | — | — | 295 | 4.28 | — | — | 114 |
| 2-OH | 251 | 4.04 | — | — | 342 | 3.20 | 89 |
| 2-OMe | 251 | 4.04 | — | — | 342 | 3.20 | 89 |
| 3-OMe | 256 | 4.05 | — | — | — | — | 89 |
| 2,4-di-OH | 242 | 3.94 | 290 | 3.96 | 338 | 4.12 | 114 |
| 2,6-di-OH | 250 | 4.07 | 280 | 3.74 | — | — | 114 |
| 2,6-di-OH-5- ϕ CO | 248 | 4.30 | 290 | 3.90 | 348 | 4.34 | 114 |
| 2,4-di-OH-5- ϕ CO | 258 | 4.27 | 275 | 4.26 | 338 | 4.15 | 114 |
| 2,6-di-OH-3,5-di- ϕ CO | 258 | 4.30 | 280 | 4.53 | 330 | 3.91 | 114 |
| 2,4-di-OH-4'-OMe | 256 | 4.16 | 285 | 4.29 | 325 | 4.14 | 114 |
| 2,4-di-OH-4'-Me | 250 | 3.93 | 290 | 4.07 | 340 | 4.09 | 114 |
| 2,4-di-OH-4'-Cl | 250 | 4.08 | 290 | 4.02 | 325 | 4.04 | 114 |
| 2,4-di-OH-3',4'-di-Cl | 252 | 3.98 | 290 | 4.10 | 325 | 3.96 | 114 |
| 2,4-di-OH-2',4'-di-OH | 242 | 3.80 | 283 | 3.96 | 352 | 4.17 | 114 |
| 2,4-di-OMe | 245 | 4.18 | 280 | 3.86 | 310 | 3.78 | 114 |
| 2-OH-4-OMe | — | — | 289 | 4.13 | 322 | 3.96 | 114 |
| 2-OH-4,4'-di-OMe | — | — | 285 | 4.20 | 320 | 4.12 | 114 |
| 2-OH-4-OMe-3-Me | 250 | 3.89 | 300 | 4.27 | — | — | 114 |